

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 May 2004 (06.05.2004)

PCT

(10) International Publication Number
WO 2004/037837 A1

(51) International Patent Classification⁷: **C07F 15/00**,
15/02, 15/04, 15/06, C08F 10/00, 4/00, 2/00

European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(21) International Application Number:
PCT/US2003/033970

(22) International Filing Date: 24 October 2003 (24.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/421,359 25 October 2002 (25.10.2002) US
60/421,486 25 October 2002 (25.10.2002) US

(71) Applicant (for all designated States except US): **EXXON-MOBIL CHEMICAL PATENTS INC.** [US/US]; 5200 Bayway Drive, Baytown, TX 77520-2101 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ZHAO, Baiyi** [US/US]; 3014 Hickory Falls Drive, Kingwood, TX 77345 (US). **KACKER, Smita** [IN/US]; 15410 Conifer Bay Court, Houston, TX 77059 (US). **CANICH, Jo, Ann, M.** [US/US]; 15710 Mesa Verde Drive, Houston, TX 77059 (US).

(74) Agent: **BELL, Catherine, L.**; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, IIR, IU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LATE TRANSITION METAL CATALYSTS FOR OLEFIN OLIGOMERIZATIONS

(57) Abstract: A series of novel late transition metal catalysts for olefin oligomerization have been invented. The catalysts demonstrate high activity and selectivity for linear α -olefins.

WO 2004/037837 A1

Title: Late Transition Metal Catalysts For Olefin Oligomerizations**Inventors**

Baiyi Zhao, Smita Kacker and Jo Ann M. Canich

Technical Field

This document relates to late transition metal catalysts for olefin oligomerizations and to methods for making and using these catalysts.

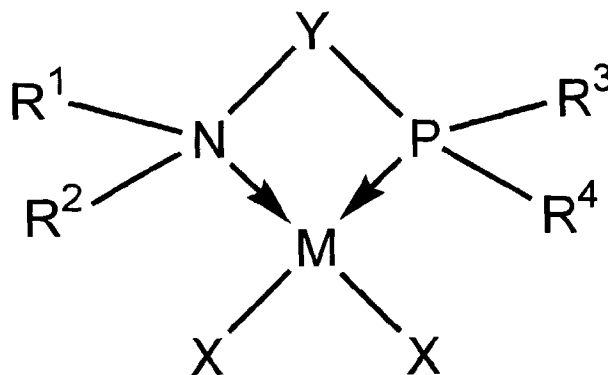
Background of the Invention

Alpha-olefins, especially those containing 6 to 20 carbon atoms, are important items of commerce. They are used as intermediates in the manufacture of detergents, as monomers (especially in linear low-density polyethylene), and as intermediates for many other types of products. Consequently, improved methods of making these compounds are desired. Especially desired, is a process capable of making a range of linear α -olefins such as 1-butene and 1-hexene.

Most commercially produced α -olefins are made by the oligomerization of ethylene, catalyzed by various types of compounds, see for instance B. Elvers, et al., Ed. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276, and B. Cornils, et al., Ed., Applied Homogeneous Catalysis with Organometallic Compounds, A Comprehensive Handbook, Vol. 1, VCH Verlagsgesellschaft mbH, Weinheim, 1996, p. 245-258. The major types of commercially used catalysts are alkylaluminum compounds, certain nickel-phosphine complexes, and a titanium halide with a Lewis acid such as $AlCl_3$. In all of these processes, significant amounts of branched internal olefins and diolefins are produced. Since in most instances these are undesirable and often difficult to separate, these byproducts are avoided commercially.

Summary

Invention catalyst systems, suitable for solution- or slurry-phase oligomerization reactions to produce α -olefins, comprise a Group-8, -9, or -10 transition metal component (catalyst precursor) and an activator. Invention catalyst precursors can be represented by the general formula:



where M is a Group-8, -9, or -10 transition metal, especially Fe, Co and Ni; N is nitrogen; P is phosphorous; Y is a hydrocarbyl bridge in which four or more carbon atoms connect between the nitrogen and phosphorus atoms; R^1 , R^2 , R^3 and R^4 are independently hydrocarbyl radicals such as C_1 - C_{40} aliphatic radicals, C_3 - C_{40} alicyclic radicals, C_6 - C_{40} aromatic radicals or combinations of these; X is independently a hydride radical, a hydrocarbyl radical, or hydrocarbyl-substituted organometalloid radical; or two X's are connected and form a 3 to 50 atom metallacycle ring. When Lewis-acid activators such as methylalumoxane, aluminum alkyls, alkylaluminum alkoxides or alkylaluminum halides that are capable of donating an X ligand, as described above, to the transition metal component are used, or when the ionic activator is capable of extracting X, one or more X, which may optionally be bridged to one another, may additionally be independently selected from a halogen, alkoxide, aryloxy, amide, phosphide or other anionic ligand, provided that the resulting activated catalyst contains at least one M-H or M-C bond into which an olefin can insert.

Definitions

The term "hydrocarbyl radical" is sometimes used interchangeably with "hydrocarbyl" throughout this document. For purposes of this disclosure, "hydrocarbyl radical" encompasses C₁-C₅₀ radicals. These radicals can be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Thus, the term "hydrocarbyl radical", in addition to unsubstituted hydrocarbyl radicals, encompasses substituted hydrocarbyl radicals, halocarbyl radicals, and substituted halocarbyl radicals, as these terms are defined below.

Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR"₂, OR", PR"₂, SR", BR"₂, SiR"₃, GeR"₃ and the like or where at least one non-hydrocarbon atom or group has been inserted within the hydrocarbyl radical, such as O, S, NR", PR", BR", SiR"₂, GeR"₂, and the like, where R" is independently a hydrocarbyl or halocarbyl radical. The functional group can be an organometalloid radical.

Halocarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one halogen or halogen-containing group (e.g. F, Cl, Br, I).

Substituted halocarbyl radicals are radicals in which at least one hydrocarbyl hydrogen or halogen atom has been substituted with at least one functional group such as NR"₂, OR", PR"₂, SR", BR"₂, SiR"₃, GeR"₃ and the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as O, S, NR", PR", BR", SiR"₂, GeR"₂, and the like where R" is independently a hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical. The functional group can be an organometalloid radical.

In some embodiments, the hydrocarbyl radical is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl,

undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl, triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, or triacontynyl isomers. For this disclosure, when a radical is listed it indicates that radical type and all other radicals formed when that radical type is subjected to the substitutions defined above. Alkyl, alkenyl and alkynyl radicals listed include all isomers including where appropriate cyclic isomers, for example, butyl includes n-butyl, 2-methylpropyl, 1-methylpropyl, tert-butyl, and cyclobutyl (and analogous substituted cyclopropyls); pentyl includes n-pentyl, cyclopentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and neopentyl (and analogous substituted cyclobutyls and cyclopropyls); butenyl includes E and Z forms of 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-1-propenyl and 2-methyl-2-propenyl (and cyclobutenyls and cyclopropenyls).

The transition metal component can also be described as comprising at least one ancillary ligand that stabilizes the oxidation state of the metal. Ancillary ligands serve to enforce the geometry around the metal center. In this disclosure, ancillary ligands have a backbone that comprises nitrogen and phosphorous bridged to each other by at least 4 atoms.

For purposes of this disclosure, oligomers include about 2-75 mer units. A mer is defined as a unit of an oligomer or polymer that originally corresponded to

the olefin that was used in the polymerization reaction. For example, the mer of polyethylene would be ethylene.

Abstractable ligands are ligands that are removed from the catalyst precursor to activate it. They are sometimes assigned the label X in this disclosure. X are independently hydride radicals, hydrocarbyl radicals, or hydrocarbyl-substituted organometalloid radicals; or two X's are connected and form a 3-to-50-atom metallacycle ring. When Lewis-acid activators such as methylalumoxane, aluminum alkyls, alkylaluminum alkoxides or alkylaluminum halides that are capable of donating an X ligand, as described above, to the transition metal component are used, or when the ionic activator is capable of extracting X, one or more X, which may optionally be bridged to one another, may additionally be independently selected from a halogen, alkoxide, aryloxy, amide, phosphide or other anionic ligand, provided that the resulting activated catalyst contains at least one M-H or M-C connection in which an olefin can insert.

In some structures throughout this specification the ligand-metal connection is drawn with an arrow indicating that the electrons originally came from the ligand. At other times, connection is shown by drawing a solid line. One of ordinary skill in the art recognizes that these depictions are interchangeable.

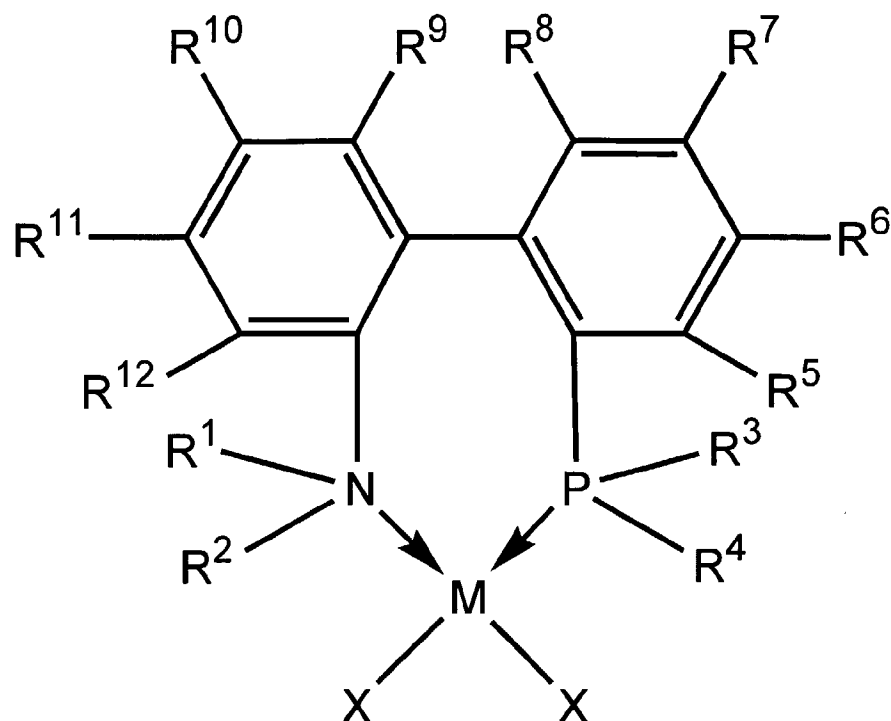
C_6F_5 is pentafluorophenyl or perfluorophenyl.

For purposes of this document, the term "comprising" is interchangeable with "including".

Detailed Description

In one embodiment of this invention, the catalyst precursor can be represented by the following formula:

-6-



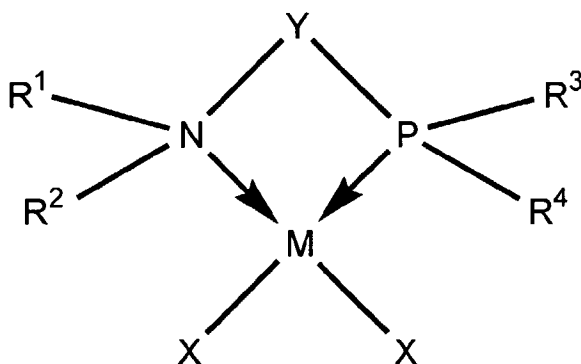
where M , N , P , R^1 , R^2 , R^3 , R^4 and X are defined above, and R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , and R^{12} are independently hydrogen, fluorine, or C_1 - C_{20} hydrocarbyl radicals. The organic group connecting between N and P takes the place of Y , the hydrocarbyl bridge.

In other invention embodiments, R^1 and R^2 are independently C_1 - C_{12} hydrocarbyl radicals, C_1 - C_6 hydrocarbyl radicals, or methyl radicals. In these or other embodiments, R^3 and R^4 are independently C_6 - C_{20} hydrocarbyl radicals, C_6 - C_{12} hydrocarbyl radicals, aromatic radicals, cyclohexyl radicals, or phenyl radicals.

Specific, invention catalyst precursor examples are illustrated by the following formula where some components are listed in Table 1. For Y , alkylenes are diradicals and include all isomers of bridge length 4 or greater, for example, hexylene includes 1,6-hexylene, 2,5-hexylene, 2-methyl-1,5-pentylene, 3-methyl-1,5-pentylene, 4-methyl-1,5-pentylene, 1,5-hexylene, 3,6-hexylene, 2-ethyl-1,4-butylene, 3-ethyl-1,4-butylene, 4-ethyl-1,4-butylene, and 1,4-hexylene. To illustrate members of the transition metal component, select any combination

-7-

listed in Table 1. For example, by choosing the first row components, the transition metal compound would be 1-(N,N-dimethylamino)-4-(P,P-dimethylphosphino)butylene nickel dichloride. By selecting a combination of components from Table 1, an example would be 2-(N,N-dimethylamino)-2'-(P,P-dicyclohexylphosphino)biphenyl nickel dibromide. Any combination of components may be selected.

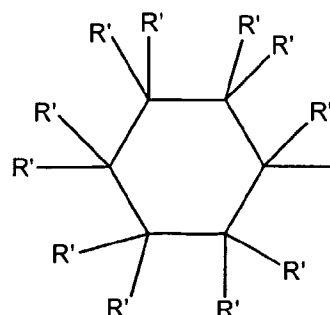
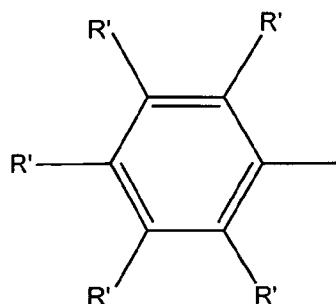


R ¹ , R ² , R ³ , and R ⁴	Y	X ¹ and X ²	M
Methyl	butylene	chloride	nickel
Ethyl	pentylene	bromide	iron
Propyl	hexylene	iodide	cobalt
Butyl	heptylene	methyl	palladium
Pentyl	octylene	ethyl	platinum
Hexyl	nonylene	propyl	ruthenium
Heptyl	decylene	butyl	osmium
Octyl	undecylene	pentyl	rhodium
Nonyl	dodecylene	hexyl	iridium
Decyl	tridecylene	heptyl	
Undecyl	tetradecylene	octyl	
Dodecyl	pentadecylene	nonyl	
Tridecyl	hexadecylene	decyl	
Tetradecyl	heptadecylene	undecyl	
Pentadecyl	octadecylene	dodecyl	

Hexadecyl	nonadecylene	tridecyl	
Heptadecyl	eicosylene	tetradecyl	
Octadecyl	heneicosylene	pentadecyl	
Nonadecyl	docosylene	hexadecyl	
Eicosyl	tricosylene	heptadecyl	
Heneicosyl	tetracosylene	octadecyl	
Docosyl	pentacosylene	nonadecyl	
Tricosyl	hexacosylene	eicosyl	
Tetracosyl	heptacosylene	heneicosyl	
Pentacosyl	octacosylene	docosyl	
Hexacosyl	nonacosylene	tricosyl	
Heptacosyl	triacontylene	tetracosyl	
Octacosyl	cyclohexylene	pentacosyl	
Nonacosyl	cyclooctylene	hexacosyl	
Triacetyl	cyclodecylene	heptacosyl	
Ethenyl	cyclododecylene	octacosyl	
Propenyl	2,2'-biphenyl	nonacosyl	
Butenyl	butenylene	triacontyl	
Pentenyl	penentylene	hydride	
Hexenyl	hexenylene	phenyl	
Heptenyl	heptenylene	benzyl	
Octenyl	octenylene	phenethyl	
Nonenyl	nonenylene	tolyl	
Decenyl	decenylene	methoxy	
Undecenyl	undecenylene	ethoxy	
Dodecenyl	dodecenylene	propoxy	
Ethynyl	hexynylene	butoxy	
Propynyl	heptynylene	dimethylamino	
Butynyl	octynylene	diethylamino	
Pentynyl	nonynylene	methylethylamino	
Hexynyl	decynylene	phenoxy	
Heptynyl	undecynylene	benzoxy	

Octynyl	dodecynylene	allyl	
Nonyl	butadienylene	1,1-dimethyl allyl	
Decynyl	pentadienylene	2-carboxymethyl allyl	
Undecynyl	hexadienylene	acetylacetonate	
Dodecynyl	heptadienylene	1,1,1,5,5,5-hexa-fluoroacetylacetonate	
Phenyl	octadienylene	1,1,1-trifluoro-acetylacetonate	
Benzyl	nonadienylene	1,1,1-trifluoro-5,5-di-methylacetylacetonate	
Phenethyl	decadienylene		
Tolyl	undecadienylene	both X ¹ and X ²	
Cyclobutyl	dodecadienylene	catecholate	
Cyclopentyl	hexatrienylene	3,5-dibutylcatecholate	
Cyclohexyl	octatrienylene	3,6-dibutylcatecholate	
Cycloheptyl	decatrienylene	3,6-dibutyl-4,5-dimethoxycatecholate	
Cyclooctyl	dodecatrienylene	3,6-dibutyl-4,5-dichlorocatecholate	
Cyclononyl		3,6-dibutyl-4,5-dibromocatecholate	
Cyclodecyl		1,3-propylene	
Cyclododecyl		1,4-butylene	

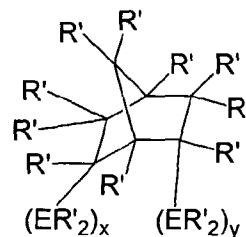
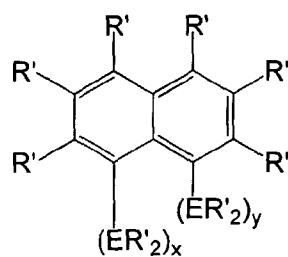
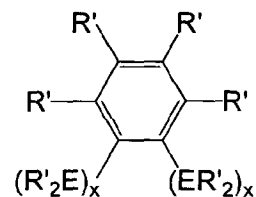
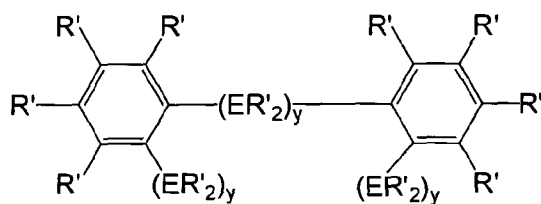
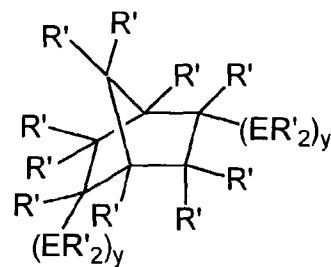
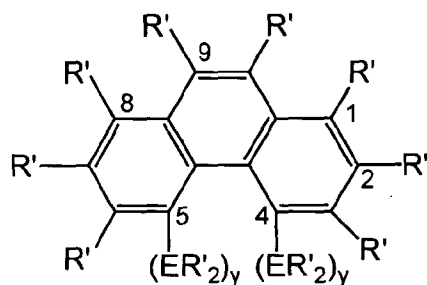
R³ and R⁴ can further independently be defined as one of the following substituents:



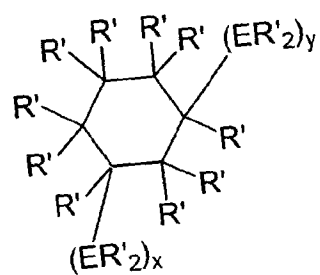
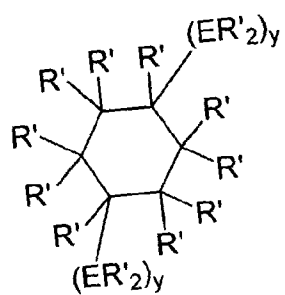
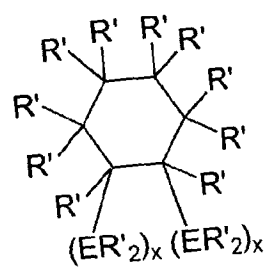
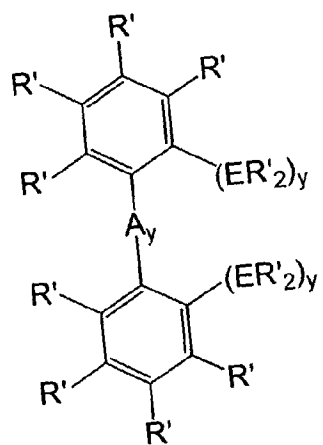
where R' are independently, hydrogen or C_1 - C_{50} hydrocarbyl radicals.

Additionally, any two adjacent R' may independently be joined to form a saturated or unsaturated cyclic structure.

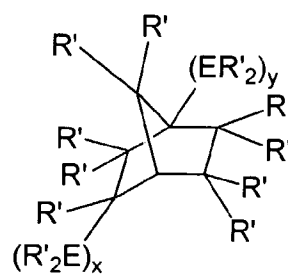
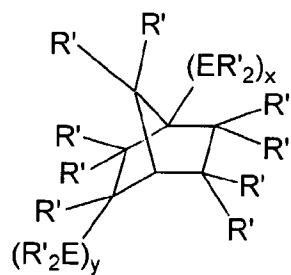
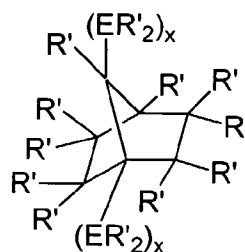
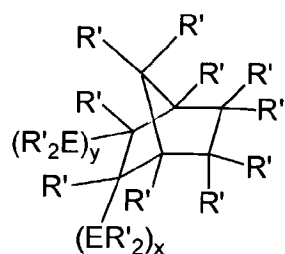
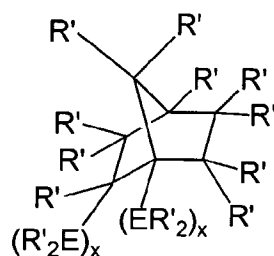
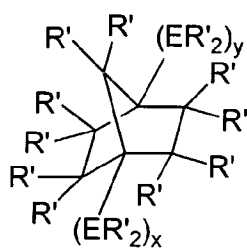
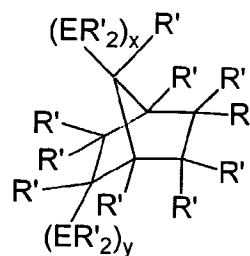
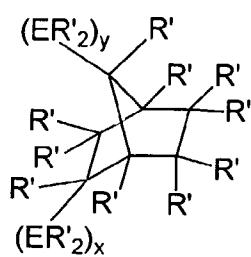
Y can further be defined as one of the following bridging groups:



-11-



-12-



where R' is as defined above, A is a non-hydrocarbon atom or group (i.e. $C=O$, $C=S$, O, S, SO_2 , NR^* , PR^* , BR^* , SiR^{*}_2 , GeR^{*}_2 and the like where R^* is independently a hydrocarbyl or halocarbyl radical), E is a Group-14 element

including carbon, silicon and germanium, x is an integer from 1 to 4, and y is an integer from 0 to 4.

Common activators are useful with this invention: alumoxanes, such as methylalumoxane, modified methylalumoxane, ethylalumoxane and the like; aluminum alkyls such as trimethyl aluminum, triethyl aluminum, triisopropyl aluminum and the like; alkyl aluminum halides such as diethyl aluminum chloride and the like; and alkylaluminum alkoxides.

The alumoxane component useful as an activator typically is an oligomeric aluminum compound represented by the general formula $(R''-Al-O)_n$, which is a cyclic compound, or $R''(R''-Al-O)_nAlR''_2$, which is a linear compound. In the general alumoxane formula, R'' is independently a C_1 - C_{20} alkyl radical, for example, methyl, ethyl, propyl, butyl, pentyl, isomers thereof, and the like, and "n" is an integer from 1-50. Most preferably, R'' is methyl and "n" is at least 4. Methylalumoxane and modified methylalumoxanes are most preferred. For further descriptions see, EP 279586, EP 561476, WO94/10180 and US Pat. Nos. 4,665,208, 4,908,463, 4,924,018, 4,952,540, 4,968,827, 5,041,584, 5,103,031, 5,157,137, 5,235,081, 5,248,801, 5,329,032, 5,391,793, and 5,416,229.

The aluminum alkyl component useful as an activator is represented by the general formula $R''AlZ_2$ where R'' is defined above, and each Z is independently R'' or a different univalent anionic ligand such as halogen (Cl, Br, I), alkoxide (OR'') and the like. Most preferred aluminum alkyls include triethylaluminum, diethylaluminum chloride, triisobutylaluminum, tri-n-octylaluminum and the like.

When alumoxane or aluminum alkyl activators are used, the catalyst-precursor-to-activator molar ratio is from about 1:1000 to 10:1; alternatively, 1:500 to 1:1; or 1:300 to 1:10.

Additionally, discrete ionic activators such as $[Me_2PhNH][B(C_6F_5)_4]$, $[Bu_3NH][BF_4]$, $[NH_4][PF_6]$, $[NH_4][SbF_6]$, $[NH_4][AsF_6]$, $[NH_4][B(C_6H_5)_4]$ or Lewis acidic activators such as $B(C_6F_5)_3$ or $B(C_6H_5)_3$ can be used, if they are used in conjunction with a compound capable of alkylating the metal such as an

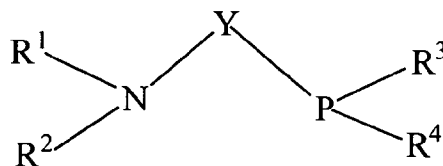
alumoxane or aluminum alkyl. Discrete ionic activators provide for an activated catalyst site and a relatively non-coordinating (or weakly coordinating) anion. Activators of this type are well known in the literature, see for instance W. Beck., et al., **Chem. Rev.**, Vol. 88, p. 1405-1421 (1988); S. H. Strauss, **Chem. Rev.**, Vol. 93, p. 927-942 (1993); US Pat. Nos. 5,198,401, 5,278,119, 5,387,568, 5,763,549, 5,807,939, 6,262,202, and WO93/14132, WO99/45042 WO01/30785 and WO01/42249.

Invention catalyst precursors can also be activated with cocatalysts or activators that comprise non-coordinating anions containing metalloid-free cyclopentadienide ions. These are described in U.S. Patent Publication 2002/0058765 A1, published on 16 May 2002.

When a discrete ionic activator is used, the catalyst-precursor-to-activator molar ratio is from 1:10 to 1.2:1; 1:10 to 10:1; 1:10 to 2:1; 1:10 to 3:1; 1:10 to 5:1; 1:2 to 1.2:1; 1:2 to 10:1; 1:2 to 2:1; 1:2 to 3:1; 1:2 to 5:1; 1:3 to 1.2:1; 1:3 to 10:1; 1:3 to 2:1; 1:3 to 3:1; 1:3 to 5:1; 1:5 to 1.2:1; 1:5 to 10:1; 1:5 to 2:1; 1:5 to 3:1; 1:5 to 5:1.

The catalyst-precursor-to-alkylating-agent molar ratio is from 1:10 to 10:1; 1:10 to 2:1; 1:10 to 25:1; 1:10 to 3:1; 1:10 to 5:1; 1:2 to 10:1; 1:2 to 2:1; 1:2 to 25:1; 1:2 to 3:1; 1:2 to 5:1; 1:25 to 10:1; 1:25 to 2:1; 1:25 to 25:1; 1:25 to 3:1; 1:25 to 5:1; 1:3 to 10:1; 1:3 to 2:1; 1:3 to 25:1; 1:3 to 3:1; 1:3 to 5:1; 1:5 to 10:1; 1:5 to 2:1; 1:5 to 25:1; 1:5 to 3:1; 1:5 to 5:1.

The catalyst systems of this invention can additionally be prepared by combining in any order, the bidentate ligand:



where N, P, Y, R¹, R², R³ and R⁴ are as previously defined and a Group-8, -9, or -10 halide salt which may optionally be coordinated by solvent (for example

NiX_2 or $\text{NiX}_2 \cdot \text{MeOCH}_2\text{CH}_2\text{OMe}$ where $\text{X} = \text{Cl, Br or I}$) in an activator-compound solution (for example methylalumoxane dissolved in toluene). The reactants may be added in any order, or even essentially simultaneously.

Invention catalyst precursor solubility allows for the ready preparation of supported catalysts. To prepare uniform supported catalysts, the catalyst precursor should significantly dissolve in the chosen solvent. The term "uniform supported catalyst" means that the catalyst precursor or the activated catalyst approach uniform distribution upon the support's accessible surface area, including the interior pore surfaces of porous supports.

Invention supported catalyst systems may be prepared by any method effective to support other coordination catalyst systems, effective meaning that the catalyst so prepared can be used for oligomerizing olefin in a heterogeneous process. The catalyst precursor, activator, suitable solvent, and support may be added in any order or simultaneously. In one invention embodiment, the activator, dissolved in an appropriate solvent such as toluene is stirred with the support material for 1 minute to 10 hours. The total volume of the activation solution may be greater than the pore volume of the support, but some embodiments limit the total solution volume below that needed to form a gel or slurry (about 100-200% of the pore volume). The mixture is optionally heated to 30-200°C during this time. The catalyst can be added to this mixture as a solid, if a suitable solvent is employed in the previous step, or as a solution. Or alternatively, this mixture can be filtered, and the resulting solid mixed with a catalyst precursor solution. Similarly, the mixture may be vacuum dried and mixed with a catalyst precursor solution. The resulting catalyst mixture is then stirred for 1 minute to 10 hours, and the catalyst is either filtered from the solution and vacuum dried, or vacuum or evaporation alone removes the solvent.

In another invention embodiment, the catalyst precursor and activator are combined in solvent to form a solution. The support is then added to this solution and the mixture is stirred for 1 minute to 10 hours. The total volume of this solution may be greater than the pore volume of the support, but some

embodiments limit the total solution volume below that needed to form a gel or slurry (about 100-200% pore volume). The residual solvent is then removed under vacuum, typically at ambient temperature and over 10-16 hours. But greater or lesser times are possible.

The catalyst precursor may also be supported in the absence of the activator, in which case the activator is added to the liquid phase of a slurry process. For example, a solution of catalyst precursor is mixed with a support material for a period of about 1 minute to 10 hours. The resulting catalyst precursor mixture is then filtered from the solution and dried under vacuum, or vacuum or evaporation alone removes the solvent. The total volume of the catalyst precursor solution may be greater than the pore volume of the support, but some embodiments limit the total solution volume below that needed to form a gel or slurry (about 100-200% of the pore volume).

Additionally, two or more different catalyst precursors may be placed on the same support using any of the support methods disclosed above. Likewise, two or more activators may be placed on the same support.

Suitable solid particle supports typically comprise polymeric or refractory oxide materials. Some embodiments select porous supports (such as for example, talc, inorganic oxides, inorganic chlorides (magnesium chloride)) that have an average particle size greater than 10 μm . Some embodiments select inorganic oxide materials as the support material including Group-2, -3, -4, -5, -13, or -14 metal or metalloid oxides. Some embodiments select the catalyst support materials to include silica, alumina, silica-alumina, and their mixtures. Other inorganic oxides may serve either alone or in combination with the silica, alumina, or silica-alumina. These are magnesia, titania, zirconia, and the like. Lewis acidic materials such as montmorillonite and similar clays may also serve as a support. In this case, the support can optionally double as the activator component. But additional activator may also be used.

As well known in the art, the support material may be pretreated by any number of methods. For example, inorganic oxides may be calcined, and/or chemically treated with dehydroxylating agents such as aluminum alkyls and the like.

Some embodiments select the carrier of invention catalysts to have a surface area of 10-700 m²/g, or pore volume of 0.1-4.0 cc/g, and average particle size from 10-500 μ m. But greater or lesser values may also be used.

Invention catalysts may generally be deposited on the support at a loading level of 10-100 micromoles of catalyst precursor per gram of solid support; alternately from 20-80 micromoles of catalyst precursor per gram of solid support; or from 40-60 micromoles of catalyst precursor per gram of support. But greater or lesser values may be used. Some embodiments select greater or lesser values, but require that the total amount of solid catalyst precursor does not exceed the support's pore volume.

Additionally, oxidizing agents may be added to the supported or unsupported catalyst as described in WO 01/68725.

Process

In the invention oligomerization processes, the process temperature may be -100°C to 300°C, -20°C to 200°C, or 0°C to 150°C. Some embodiments select ethylene oligomerization pressures (gauge) from 0 kPa-35 MPa or 500 kPa-15 MPa.

The preferred and primary feedstock for the oligomerization process is the α -olefin, ethylene. But other α -olefins, including but not limited to propylene and 1-butene, may also be used alone or combined with ethylene.

Invention oligomerization processes may be run in the presence of various liquids, particularly aprotic organic liquids. The homogeneous catalyst system,

ethylene, α -olefins, and product are soluble in these liquids. A supported (heterogeneous) catalyst system may also be used, but will form a slurry rather than a solution. Suitable liquids for both homo- and heterogeneous catalyst systems, include alkanes, alkenes, cycloalkanes, selected halogenated hydrocarbons, aromatic hydrocarbons, and in some cases, hydrofluorocarbons. Useful solvents specifically include hexane, toluene, cyclohexane, and benzene.

Also, mixtures of α -olefins containing desirable numbers of carbon atoms may be obtained. Factor K from the Schulz-Flory theory (see for instance B. Elvers, et al., Ed. **Ullmann's Encyclopedia of Industrial Chemistry**, Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276) serves as a measure of these α -olefins' molecular weights. From this theory,

$$K = n(C_{n+2} \text{ olefin})/n(C_n \text{ olefin})$$

where $n(C_n \text{ olefin})$ is the number of moles of olefin containing n carbon atoms, and $n(C_{n+2} \text{ olefin})$ is the number of moles of olefin containing n+2 carbon atoms, or in other words the next higher oligomer of C_n olefin. From this can be determined the weight (mass) fractions of the various olefins in the resulting product. The ability to vary this factor provides the ability to choose the then-desired olefins.

Invention-made α -olefins may be further polymerized with other olefins to form polyolefins, especially linear low-density polyethylenes, which are copolymers containing ethylene. They may also be homopolymerized. These polymers may be made by a number of known methods, such as Ziegler-Natta-type polymerization, metallocene catalyzed polymerization, and other methods, see for instance WO 96/23010, see for instance **Angew. Chem., Int. Ed. Engl.**, vol. 34, p. 1143-1170 (1995); European Patent Application, 416,815; and U.S. Patent 5,198,401 for information about metallocene-type catalysts, and J. Boor Jr., **Ziegler-Natta Catalysts and Polymerizations**, Academic Press, New York, 1979 and G. Allen, et al., Ed., **Comprehensive Polymer Science**, Vol. 4, Pergamon Press, Oxford, 1989, pp. 1-108, 409-412 and 533-584, for information about

Ziegler-Natta-type catalysts, and H. Mark, et al., Ed., **Encyclopedia of Polymer Science and Engineering**, Vol. 6, John Wiley & Sons, New York, 1992, p. 383-522, for information about polyethylene.

Invention-made α -olefins may be converted to alcohols by known processes, these alcohols being useful for a variety of applications such as intermediates for detergents or plasticizers. The α -olefins may be converted to alcohols by a variety of processes, such as the oxo process followed by hydrogenation, or by a modified, single-step oxo process (the modified Shell process), see for instance B. Elvers, et al., Ed., **Ullmann's Encyclopedia of Chemical Technology**, 5th Ed., Vol. A18, VCH Verlagsgesellschaft mbH, Weinheim, 1991, p. 321-327.

A set of exemplary catalyst precursors is set out below. These are by way of example only and are not intended to list every catalyst precursor that is within the scope of the invention.

Several structures are shown along with their corresponding name.

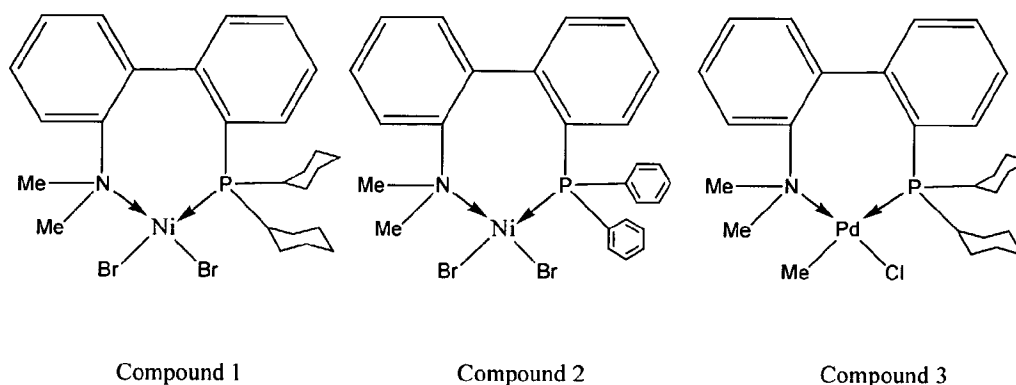
Examples

The following examples are presented to illustrate the discussion above. Although the examples may be directed toward certain embodiments of the present invention, they do not limit the invention in any specific way. In these examples, certain abbreviations are used to facilitate the description. These include standard chemical abbreviations for the elements and certain, commonly accepted abbreviations, such as: Me = methyl, Ph = phenyl, Cy = cyclohexyl, MAO = methylalumoxane, COD = cyclooctadiene and DME = ethylene glycol dimethyl ether.

All preparations were performed under an inert nitrogen atmosphere using standard Schlenk or glovebox techniques, unless mentioned otherwise. Dry solvents (toluene, diethyl ether, pentane, methylene chloride) were purchased as

anhydrous solvents and further purified by passing them down an alumina (Fluka) column. Ethylene (99.9%) was purchased from BOC (Surrey, United Kingdom). 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl and 2-(N,N-dimethylamino)-2'-(diphenylphosphino)biphenyl were purchased from Strem Chemicals, Inc. Tetramethyltin, nickel(II) bromide ethylene glycol dimethylether complex, and dichloro(1,5-cyclooctadiene)palladium(II) were purchased from Aldrich Chemical Company. Deuterated solvents were dried with CaH and vacuum distilled prior to use.

Some compounds prepared are illustrated below:

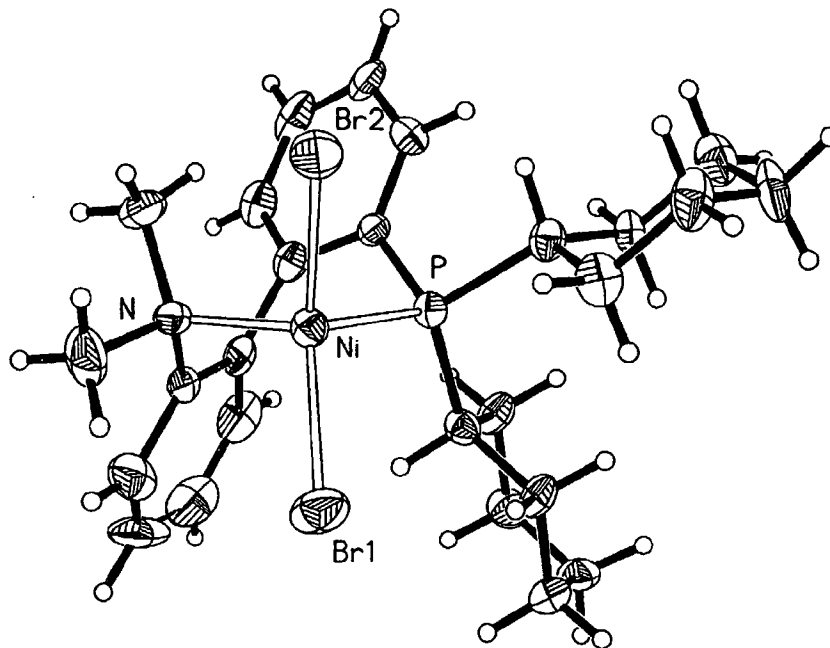


Preparation of 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl nickel dibromide (compound 1).

CH₂Cl₂ (25 ml) was added to a Schlenk flask containing 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl (2.00 g, 5.10 mmol) and (DME)NiBr₂ (1.23 g, 4.0 mmol) in a dry box. A dark blue solution formed immediately upon mixing. This solution was stirred for 20 hours. Then, it was filtered and recrystallized from CH₂Cl₂/pentane. The product was washed three times with an additional 15 ml of pentane and dried for 1 hour under vacuum. A blue powder was isolated in 49.0% yield. The product was soluble in CH₂Cl₂. ¹H NMR indicates that it is paramagnetic. Anal. Calcd for (C₂₆H₃₆NPBr₂Ni): C, 51.02%; H, 5.94%; N, 2.29%; P, 5.06%. Found: C, 50.72%; H, 6.10%; N, 2.12%;

-21-

P, 5.02%. The IR (cm^{-1} , KBr): 272, $\nu(\text{Ni-Br})$. This compound has also been characterized by x-ray crystallography.



Preparation of 2-(N,N-dimethylamino)-2'-(diphenylphosphino)biphenyl nickel dibromide (compound 2)

CH_2Cl_2 (25 ml) was added to a Schlenk flask containing the 2-(N,N-dimethylamino)-2'-(diphenylphosphino)biphenyl (2.00 g, 5.2 mmol) and $(\text{DME})\text{NiBr}_2$ (1.30 g, 4.2 mmol) in a dry box. A green solution formed immediately upon mixing. This solution was stirred for 20 hours. Then, it was filtered and recrystallized from CH_2Cl_2 /pentane. The product was washed three times with an additional 15 ml of pentane and dried for 1 hour under vacuum. A green powder was isolated in 69.3% yield. The product was soluble in CH_2Cl_2 . ^1H NMR indicates that it is paramagnetic. Anal. Calcd for $(\text{C}_{26}\text{H}_{24}\text{NPBr}_2\text{Ni})$: C, 52.03%; H, 4.08%; N, 2.33%; P, 5.16%. Found: C, 48.12%; H, 4.24%; N, 2.14%; P, 5.29%.

Preparation of 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl
palladium methyl chloride (compound 3)

(COD)PdCl₂ (2.0 g, 7.0 mmol) was mixed with tetramethyltin (1.16 ml, 8.4 mmol) in CH₂Cl₂ (50 ml) at room temperature. The mixture was stirred overnight until the bright yellow color of the precursor had vanished. The resulting mixture was filtered through Celite yielding a pale yellow solution. The solvent was removed from the that solution, leaving behind an off-white solid, (COD)PdClMe, which was washed twice with diethyl ether and dried under vacuum. A solution of the white (COD)PdClMe complex (0.775 g, 0.0029 mol dissolved in CH₂Cl₂) was reacted with 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl (1.78 g, 0.0045 mol). As a result, a light yellow palladium complex formed. ¹H NMR (250 MHz, CD₂Cl₂, δ, ppm): 0.88-2.94 m (22H, 2xC₆H₁₁); 1.06 d (3H, PdCH₃, J_{PH} = 2.5 Hz); 2.87 s (6H, 2xCH₃); 6.75-7.68 m (8H, 2xC₆H₄). Anal. Calcd for (C₂₇H₃₉NPClPd): C, 58.91%; H, 7.16%; N, 2.55%; P, 5.63%. Found: C, 59.21%; H, 7.31%; N, 2.38%; P, 5.41%.

Oligomerization Reactions

Oligomerization reactions were run in 300 mL HastelloyC Parr reactor equipped with a mechanical stirrer. Catalyst (dissolved in 75 ml toluene) was added to the reactor under argon. Ethylene was added to the reactor at 100 psig, and then the reactor was vented to maintain an atmosphere of ethylene. Methylalumoxane solution (Albemarle, 30 wt % in toluene) was then cannulated in to the reactor. This process caused catalyst activation to be completed in the presence of the monomer. After activation, the ethylene pressure was adjusted to the desired value. It was attempted to maintain the reactor temperature at room temperature; but in cases where the exotherm was very large, higher reaction temperatures were reached. After the reaction had run for an hour, the reactor was cooled in an acetone/dry ice bath and vented. The reaction was quenched with methanol. A sample of the product solution was analyzed by GC/MS after adding nonane as an internal standard. In the case of supported transition metal

compounds, silica-loaded samples were prepared by adding a solution of the transition metal complex in methylene chloride to silica followed by overnight drying of the silica under vacuum. MAO was added to the reactor solution prior to adding the supported transition metal compound. The results of the oligomerization reactions are tabulated below in Table 2.

Table 2: Oligomerization Examples

Catalyst ^a	C ₂ (psig)	Final Rxn Temperature (°C)	Activity (mol C ₂ / mol Ni•hr)	Product
1	820	40	226,200	Linear C ₄ to C ₁₄ (K*=0.60) ^b
1	100	30	26,700	Primarily C ₄ and C ₆ (linear)
1	800	25	155,000	Primarily C ₄ and C ₆ (linear) ^c
2	800	30	130,000	C ₄
2	100	30	8095	C ₄

^a 0.0075 mmol of catalyst

^b *K is based on C₁₄/C₁₂ molar ratio for all isomers.

^c After removing all volatiles at room temperature under vacuum, traces of higher oligomers were observed by NMR in the residue with 84 mol % of terminal olefins; GC/MS of the same residue showed C₁₆ to C₂₄ oligomers.

While certain representative embodiments and details have been shown to illustrate the invention, it will be apparent to skilled artisans that various process and product changes from those currently disclosed may be made without

departing from this invention's scope. The appended claims define the invention's scope.

All cited patents, test procedures, priority documents, and other cited documents are fully incorporated by reference to the extent that this material is consistent with this specification and for all jurisdictions in which such incorporation is permitted.

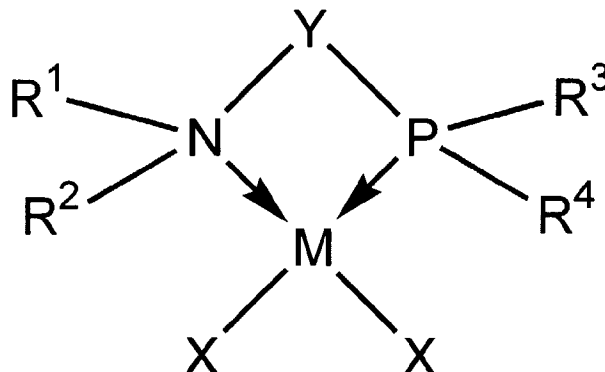
Certain features of the present invention are described in terms of a set of numerical upper limits and a set of numerical lower limits. This specification discloses all ranges formed by any combination of these limits. All combinations of these limits are within the scope of the invention unless otherwise indicated.

Claims:

1. A composition of matter comprising:

- (a) a Group-8, -9, or -10 transition metal, M, excluding palladium;
- (b) an ancillary ligand comprising:
 - (i) a terminal amine comprising two independently selected hydrocarbyl radicals, R^1 and R^2 ;
 - (ii) a terminal phosphine comprising two independently selected hydrocarbyl radicals, R^3 and R^4 ; and
 - (iii) a hydrocarbyl bridge, Y, comprising a backbone wherein the hydrocarbyl bridge connects between the terminal amine and the terminal phosphine and wherein the backbone comprises a chain that is four or more carbon atoms long; and
- (c) an abstractable ligand, X.

2. The composition of matter of Claim 1 with the following formula:



wherein

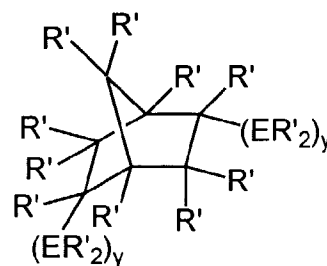
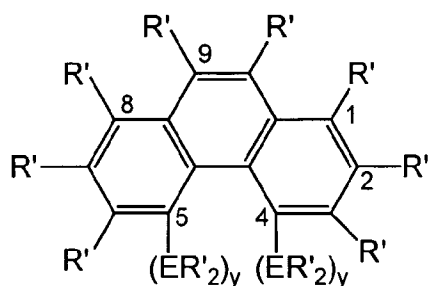
-26-

- (a) M is a Group-8, -9, or -10 transition metal, excluding palladium,
 - (b) N is nitrogen;
 - (c) P is phosphorus;
 - (d) R^1 , R^2 , R^3 , and R^4 are independently hydrocarbyl radicals;
 - (e) Y is a hydrocarbyl bridge comprising a backbone wherein the backbone comprises a chain that is four or more carbon atoms long;
 - (f) X is independently an abstractable ligand.
3. The composition of matter of Claims 1-2 wherein R^1 , R^2 , R^3 , and R^4 are independently selected from C_1 - C_{40} hydrocarbyls.
4. The composition of matter of Claim 3 wherein R^1 , R^2 , R^3 , and R^4 are independently selected from C_1 - C_{30} hydrocarbyls.
5. The composition of matter of Claim 4 wherein R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals.

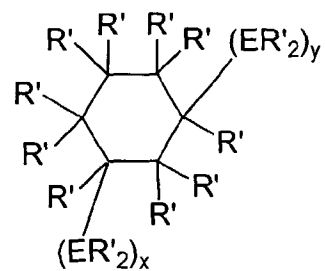
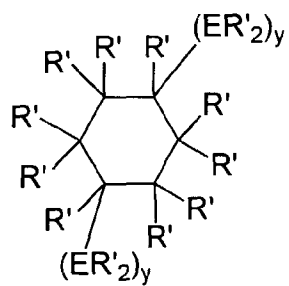
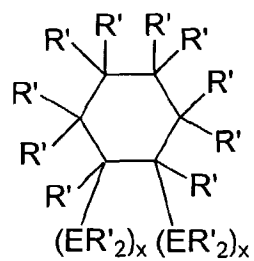
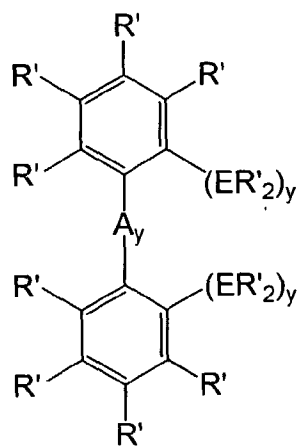
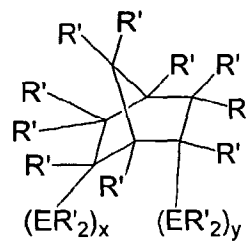
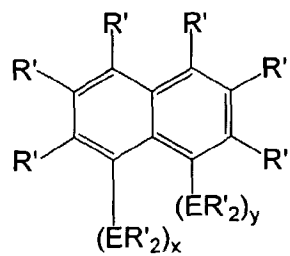
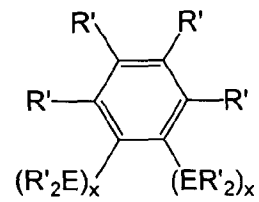
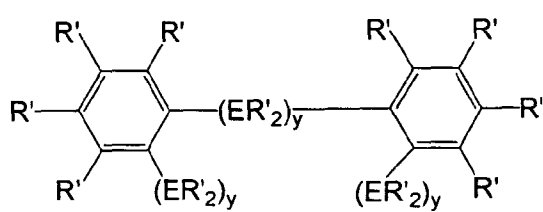
-27-

6. The composition of matter of Claim 5 wherein R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, cyclohexyl, phenyl, tolyl, benzyl, and phenethyl.
7. The composition of matter of Claims 1-6 wherein X are independently hydride radicals; hydrocarbyl radicals; hydrocarbyl-substituted, organometalloid radicals; or two X's are connected to form a 3-to-50-atom metallacycle ring.
8. The composition of matter of Claim 1-6 wherein X are independently halogen, alkoxide, aryloxy, amide, or phosphide radicals.
9. The composition of matter of Claim 8 wherein X are independently chloride, bromide, iodide, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, phenoxy, benzoxy,
10. The composition of matter of Claim 7 wherein X are independently halogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl,
11. The composition of matter of Claim 1-6 wherein X are independently allyl, 1,1-dimethyl allyl, 2-carboxymethyl allyl, acetylacetonate, 1,1,1,5,5,5-hexafluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-dimethylacetylacetonate radicals.
12. The composition of matter of Claims 1-9 wherein M is selected from nickel, iron, cobalt, platinum, ruthenium, osmium, rhodium, and iridium.
13. The composition of matter of Claim 12 wherein M is selected from iron, nickel, and cobalt.

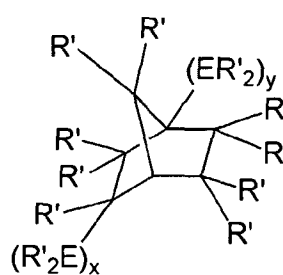
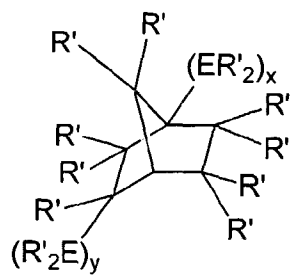
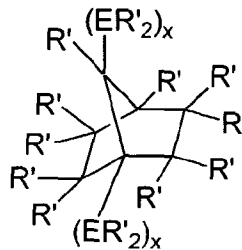
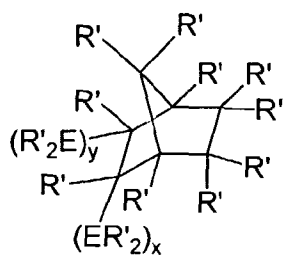
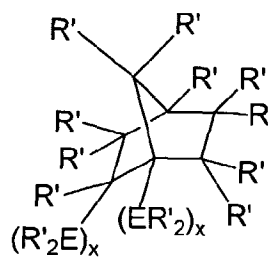
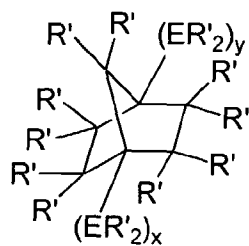
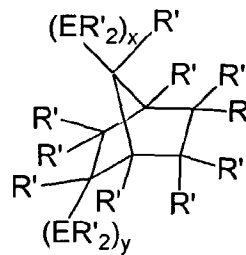
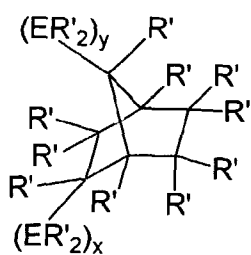
14. The composition of matter of Claims 1-13 wherein Y is selected from butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, tridecylene, tetradecylene, pentadecylene, hexadecylene, heptadecylene, octadecylene, nonadecylene, eicosylene, heneicosylene, docosylene, tricosylene, tetracosylene, pentacosylene, hexacosylene, heptacosylene, octacosylene, nonacosylene, triacontylene, cyclohexylene, cyclooctylene, cyclododecylene, cyclododecylene, biphenyl, butenylene, penentylene, hexenylene, heptenylene, octenylene, nonenylene, decenylene, undecenylene, dodecenylene, hexynylene, heptynylene, octynylene, nonynylene, decynylene, undecynylene, dodecynylene, butadienylene, pentadienylene, hexadienylene, heptadienylene, octadienylene, nonadienylene, decadienylene, undecadienylene, dodecadienylene, hexatrienylene, octatrienylene, decatrienylene, and dodecatrienylene radicals.
15. The composition of matter of 14 wherein Y is selected from biphenyl.
16. The composition of matter of 14 wherein Y has one of the following formulas:



-29-



-30-



where

- (a) R' are independently, hydrogen or C_1 - C_{50} hydrocarbyl radicals;

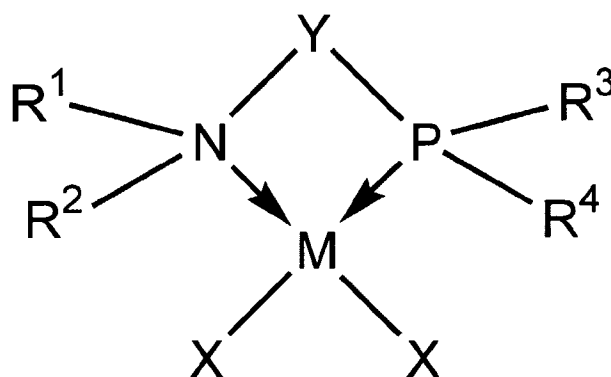
-31-

- (b) A is a non-hydrocarbon atom functional group;
- (c) E is a Group-14 element;
- (d) x is an integer from 1 to 4; and
- (e) y is an integer from 0 to 4.

17. The composition of Claim 16 wherein A is selected from C=O, C=S, O, S, SO₂, NR*, PR*, BR*, SiR*₂, and GeR*₂ wherein R* is independently a hydrocarbyl or halocarbyl radical.
18. A composition of matter comprising the reaction product of an activator and the composition of matter of any of Claims 1-17.
19. A composition of matter comprising the reaction product of
- (a) the composition of matter of Claim 18 and
 - (b) ethylene, propylene, 1-butene, or a mixture of any two or all three of ethylene, propylene, and 1-butene.
20. A polymerization method comprising the step of providing at least one composition of matter of Claims 1-19.
21. The polymerization method of Claim 16 wherein the catalysts activity exceeds 8000 moles of ethylene per mole transition metal per hour
22. The polymerization method of any of Claims 20 or 21 further comprising recovering a product comprising greater than 50 wt% of linear C₄-C₁₄ α-olefins based on the total weight of polymerized product.
23. The polymerization method of Claim 22 wherein the product comprises greater than 80 wt% of linear C₄-C₁₄ α-olefins.

-32-

24. The polymerization method of Claim 23 wherein the product comprises greater than 50 wt% of linear C₄ and C₆ α -olefins.
25. The polymerization method of Claim 24 wherein the product comprises greater than 80 mol% of linear C₄ and C₆ α -olefins.
26. A composition of matter comprising the reaction product of:
- (a) an activator; and
 - (b) a catalyst precursor with the following formula:



wherein

- (i) M is iron, nickel, cobalt, and palladium;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R¹, R², R³, and R⁴ are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl,

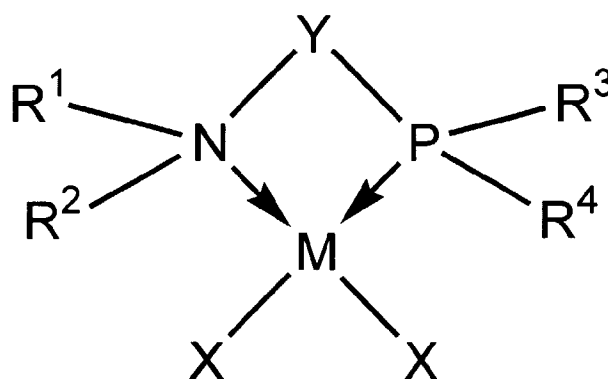
-33-

hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;

- (v) Y is a hydrocarbyl bridge comprising a backbone wherein the backbone comprises a chain that is four or more carbon atoms long;
- (vi) X are independently abstractable ligands.

27. A composition of matter comprising the reaction product of:

- (a) an activator; and
- (b) a catalyst precursor with the following formula:



wherein

- (i) M is from nickel, iron, cobalt, palladium, platinum, ruthenium, osmium, rhodium, and iridium;
- (ii) N is nitrogen;

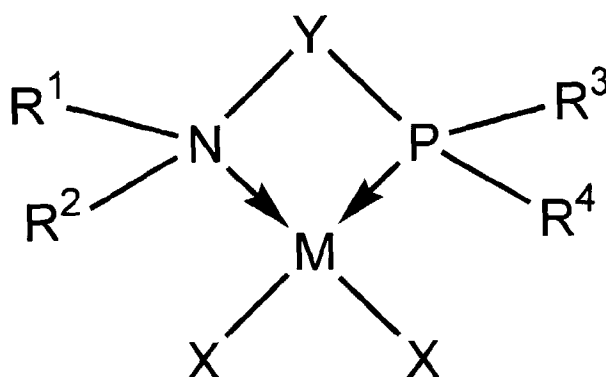
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;
- (v) Y is a hydrocarbyl bridge comprising a backbone wherein the backbone comprises a chain that is four or more carbon atoms long; and
- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-di-

-35-

methylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

28. A composition of matter comprising the reaction product of:

- (a) an activator; and
- (b) a catalyst precursor with the following formula:



wherein

- (i) M is from nickel, iron, cobalt, palladium, platinum, ruthenium, osmium, rhodium, and iridium;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl,

dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;

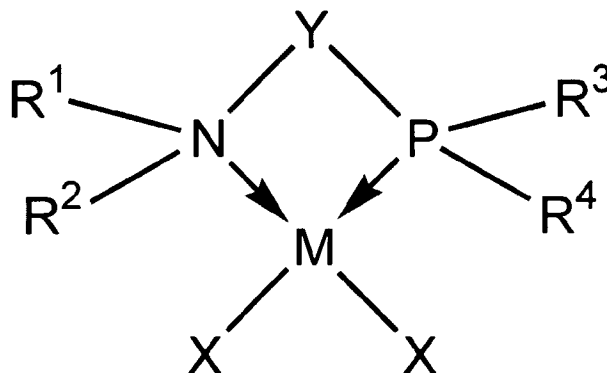
- (v) Y is selected from butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, tridecylene, tetradecylene, pentadecylene, hexadecylene, heptadecylene, octadecylene, nonadecylene, eicosylene, heneicosylene, docosylene, tricosylene, tetracosylene, pentacosylene, hexacosylene, heptacosylene, octacosylene, nonacosylene, triacontylene, cyclohexylene, cyclooctylene, cyclodecylene, cyclododecylene, biphenyl, butenylene, pentenylene, hexenylene, heptenylene, octenylene, nonenylene, decenylene, undecenylene, dodecenylene, hexynylene, heptynylene, octynylene, nonynylene, decynylene, undecynylene, dodecynylene, butadienylene, pentadienylene, hexadienylene, heptadienylene, octadienylene, nonadienylene, decadienylene, undecadienylene, dodecadienylene, hexatrienylene, octatrienylene, decatrienylene, and dodecatrienylene radicals; and
- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl,

-37-

methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoroacetylacetonate, or 1,1,1-trifluoro-5,5-dimethylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

29. A composition of matter comprising the reaction product of:

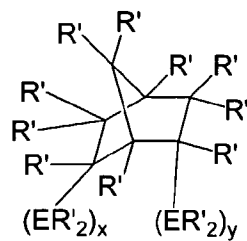
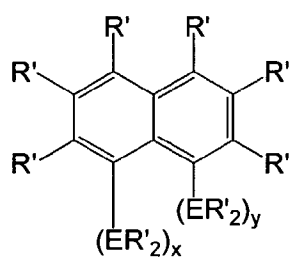
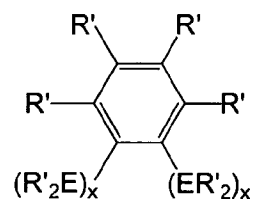
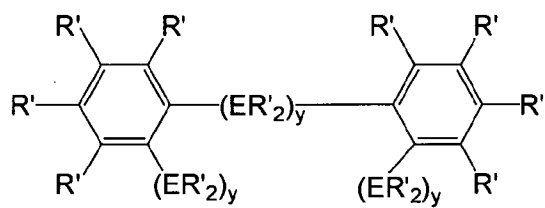
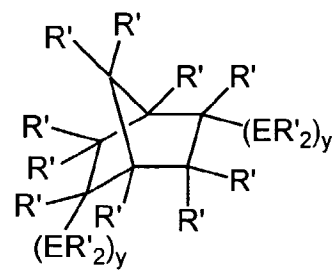
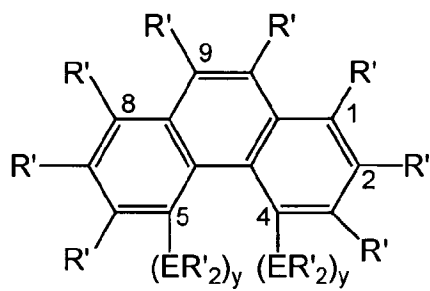
- (a) an activator; and
- (b) a catalyst precursor with the following formula:



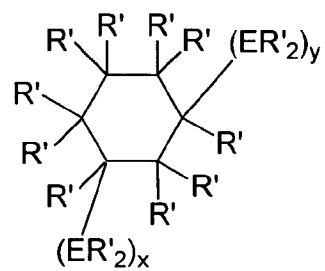
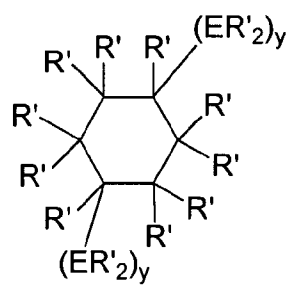
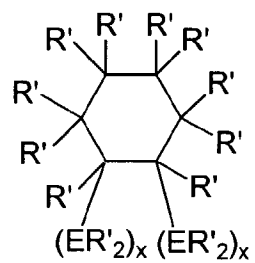
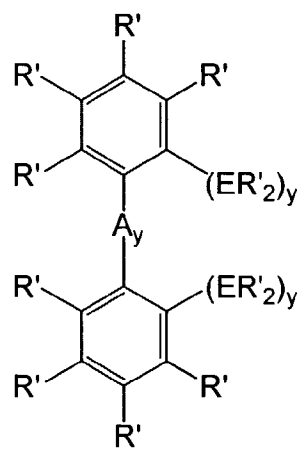
wherein

- (i) M is a Group-8, -9, or -10 transition metal;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R¹, R², R³, and R⁴ are independently hydrocarbyl radicals;
- (v) Y is represented by one of the following formulas:

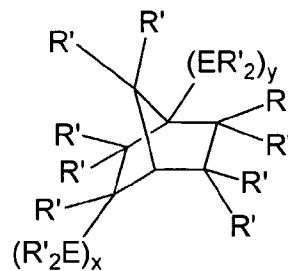
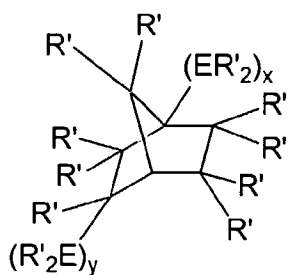
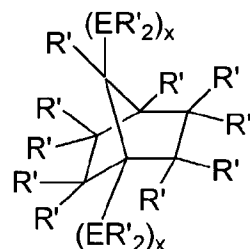
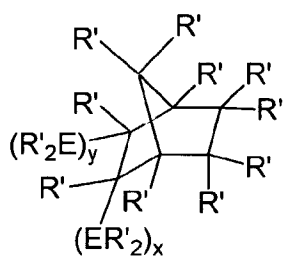
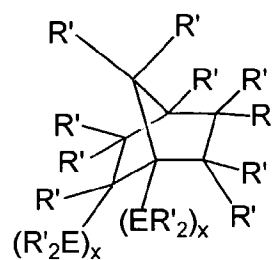
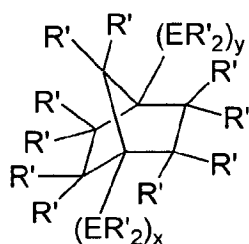
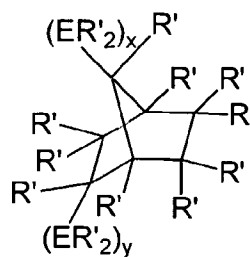
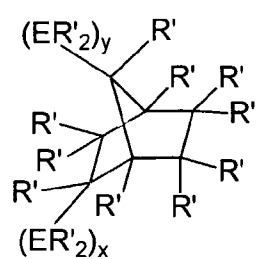
-38-



-39-



-40-



where

- R' are independently, hydrogen or C_1 - C_{50} hydrocarbyl radicals;

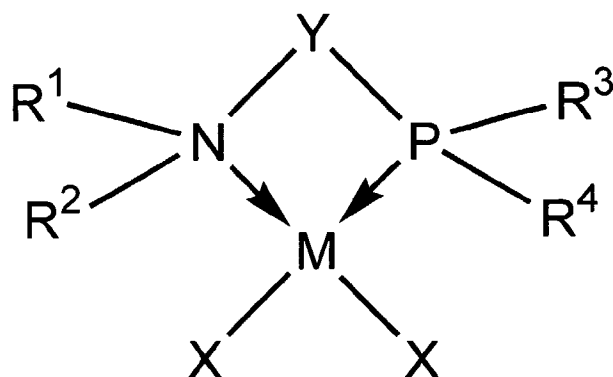
-41-

- A is a non-hydrocarbon atom functional group;
 - E is a Group-14 element;
 - x is an integer from 1 to 4; and
 - y is an integer from 0 to 4.
- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-di-methylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

30. A polymerization method wherein the catalysts activity exceeds 8000 moles of ethylene per mole transition metal per hour comprising the step of providing at least one composition of matter comprising the reaction product of:

- (a) an activator; and
- (b) a catalyst precursor with the following formula:

-42-



wherein

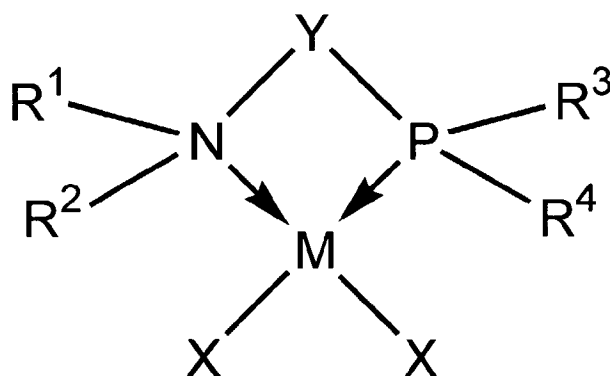
- (i) M is iron, nickel, cobalt, and palladium;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;
- (v) Y is a hydrocarbyl bridge comprising a backbone wherein the backbone comprises a chain that is four or more carbon atoms long;

-43-

(vi) X are independently abstractable ligands.

31. A polymerization method wherein the catalysts activity exceeds 8000 moles of ethylene per mole transition metal per hour comprising the step of providing at least one composition of matter comprising the reaction product of:

- (a) an activator; and
- (b) a catalyst precursor with the following formula:



wherein

- (i) M is from nickel, iron, cobalt, palladium, platinum, ruthenium, osmium, rhodium, and iridium;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl,

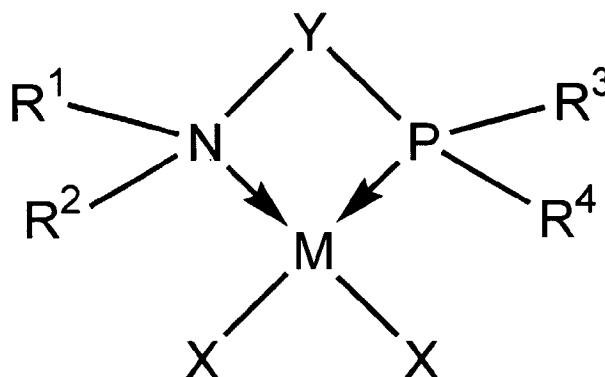
hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;

- (v) Y is a hydrocarbyl bridge comprising a backbone wherein the backbone comprises a chain that is four or more carbon atoms long; and
- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-di-methylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

32. A polymerization method wherein the catalysts activity exceeds 8000 moles of ethylene per mole transition metal per hour comprising the step of providing at least one composition of matter comprising the reaction product of:

- (a) an activator; and
- (b) a catalyst precursor with the following formula:

-45-



wherein

- (i) M is from nickel, iron, cobalt, palladium, platinum, ruthenium, osmium, rhodium, and iridium;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, phenyl, benzyl, phenethyl, tolyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl radicals;
- (v) Y is selected from butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, tridecylene, tetradecylene, pentadecylene,

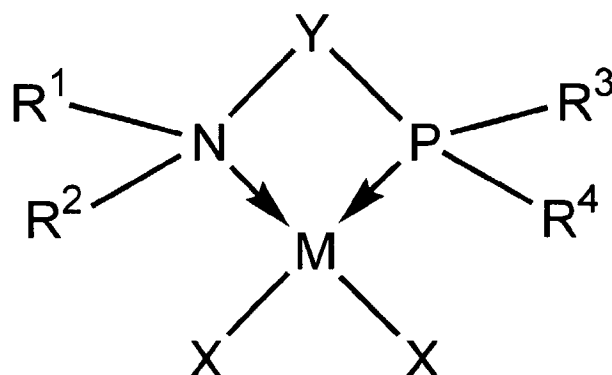
hexadecylene, heptadecylene, octadecylene, nonadecylene, eicosylene, heneicosylene, docosylene, tricosylene, tetracosylene, pentacosylene, hexacosylene, heptacosylene, octacosylene, nonacosylene, triacontylene, cyclohexylene, cyclooctylene, cyclodecylene, cyclododecylene, biphenyl, butenylene, penentylene, hexenylene, heptenylene, octenylene, nonenylene, decenylene, undecenylene, dodecenylene, hexynylene, heptynylene, octynylene, nonynylene, decynylene, undecynylene, dodecynylene, butadienylene, pentadienylene, hexadienylene, heptadienylene, octadienylene, nonadienylene, decadienylene, undecadienylene, dodecadienylene, hexatrienylene, octatrienylene, decatrienylene, and dodecatrienylene radicals; and

- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-di-methylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

-47-

33. A polymerization method wherein the catalysts activity exceeds 8000 moles of ethylene per mole transition metal per hour comprising the step of providing at least one composition of matter comprising the reaction product of:

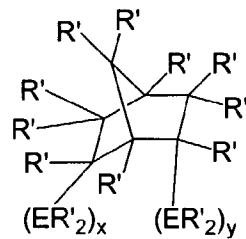
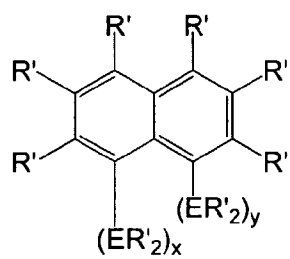
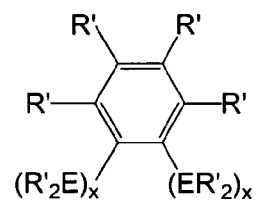
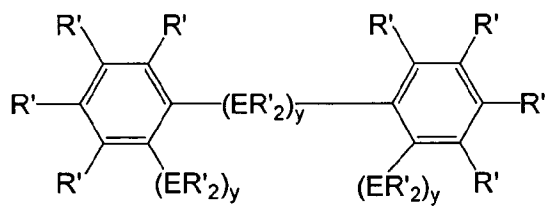
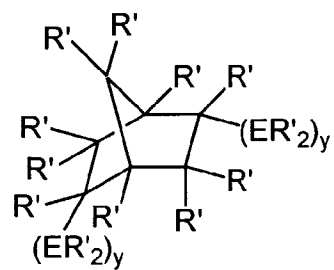
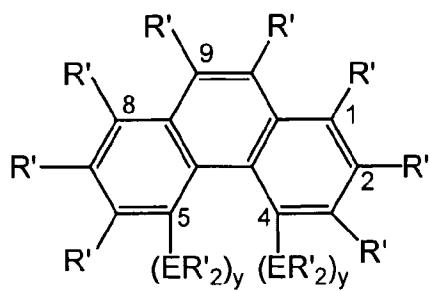
- (a) an activator; and
- (b) a catalyst precursor with the following formula:



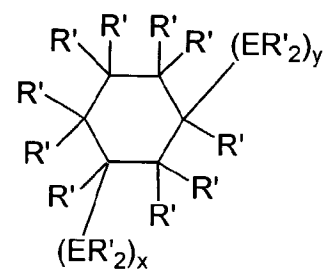
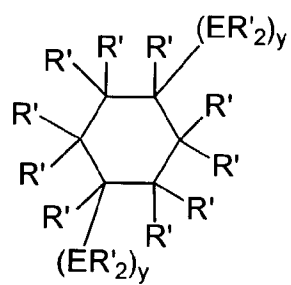
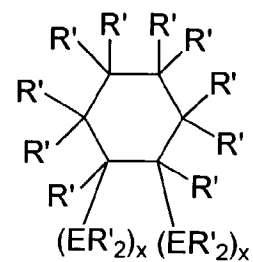
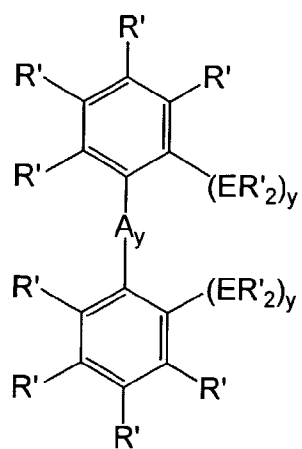
wherein

- (i) M is a Group-8, -9, or -10 transition metal;
- (ii) N is nitrogen;
- (iii) P is phosphorus;
- (iv) R^1 , R^2 , R^3 , and R^4 are independently hydrocarbyl radicals;
- (v) Y is represented by one of the following formulas:

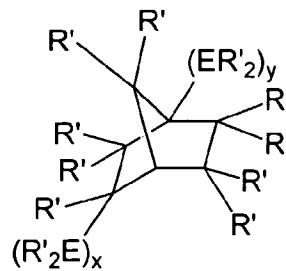
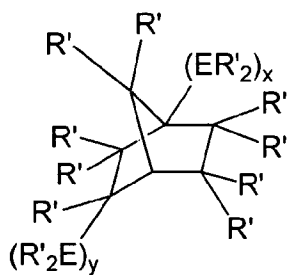
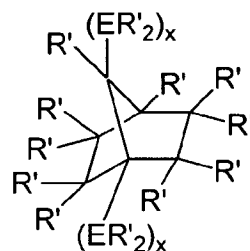
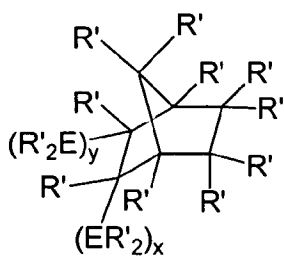
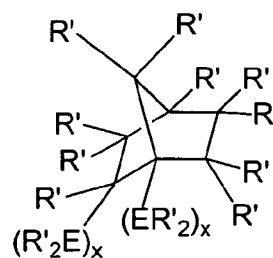
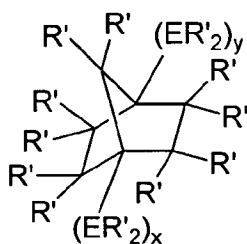
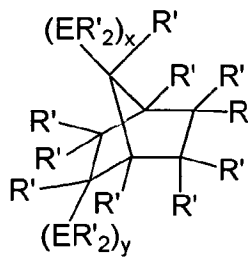
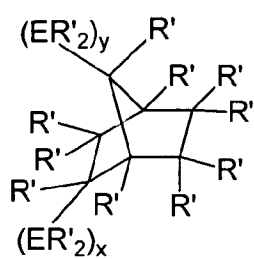
-48-



-49-



-50-



where

- R' are independently, hydrogen or C₁-C₅₀ hydrocarbyl radicals;

-51-

- A is a non-hydrocarbon atom functional group;
 - E is a Group-14 element;
 - x is an integer from 1 to 4; and
 - y is an integer from 0 to 4.
- (vi) X are independently chloride, bromide, iodide, methoxide, ethoxide, dimethylamide, diethylethoxide, phenoxide, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, hydride, phenyl, benzyl, phenethyl, tolyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, diethylamino, methylethylamino, acetylacetonate, 1,1,1,5,5,5-hexa-fluoroacetylacetonate, 1,1,1-trifluoro-acetylacetonate, or 1,1,1-trifluoro-5,5-di-methylacetylacetonate radicals; or two X's are connected to form a 3-to-40-atom metallacycle ring.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/33970

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F15/00 C07F15/02 C07F15/04 C07F15/06 C08F10/00
C08F4/00 C08F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 479 541 A (TAKASAGO INTERNATIONAL CORP., JAPAN) 8 April 1992 (1992-04-08) the whole document ---	1
X	GANDELMAN, MARK ET AL: "The First Observation and Kinetic Evaluation of a Single Step Metal Insertion into a C-C Bond" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (2000), 122(40), 9848-9849, 2000, XP002241620 the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

8 document member of the same patent family

Date of the actual completion of the international search

5 March 2004

Date of mailing of the international search report

16/03/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/33970

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KAMIGAITO, MASAMI ET AL: "Transition metal-catalyzed living radical polymerization: latest advances" retrieved from STN Database accession no. 137:338170 CA XP002241621 abstract & POLYMER PREPRINTS (AMERICAN CHEMICAL SOCIETY, DIVISION OF POLYMER CHEMISTRY) (2002), 43(2), 3-4, 2002, ---	1-33
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YORISUE, TOMOHIRO: "Polymerization catalysts for manufacture of branched polyolefins with high molecular weight and narrow molecular weight distribution" retrieved from STN Database accession no. 127:359235 CA XP002241622 abstract & JP 09 255713 A (ASAHI CHEMICAL INDUSTRY CO., LTD., JAPAN) 30 September 1997 (1997-09-30) -----	1-33

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/33970

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0479541	A	08-04-1992	JP 2739254 B2	15-04-1998
			JP 4139192 A	13-05-1992
			DE 69111358 D1	24-08-1995
			DE 69111358 T2	14-03-1996
			EP 0479541 A1	08-04-1992
			US 5159093 A	27-10-1992
			US 5210332 A	11-05-1993
<hr/>				
JP 9255713	A	30-09-1997	NONE	
<hr/>				